PATENT SPECIFICATION

746,648

Date of Application and filing Complete Specification May 5, 1954.

No. 13039/54.

Application made in United States of America on May 27, 1953.

Complete Specification Published March 14, 1956

Index at acceptance:—Class 83(4), S(2G:4).

COMPLETE SPECIFICATION

Assembly of Titanium or Titanium Alloy Parts and method of Brazing same

PATENTS ACT, 1949

SPECIFICATION NO. 746,648

In accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the eleventh day of July, 1958, this Specification has been amended under Section 33 in the following manner:-

Page 2, line 87, *after* "illustrate" *insert* "a stage during".

Page 5, line 3, *after* "layer" *insert* "completely".

Page 5, line 10, *after* "content" *insert* "of at least 13%".

Page 5, line 13, *after* "2400°F." *insert* "completely".

Page 5, line 109, *after* "is" *insert* "completely".

THE PATENT OFFICE,
24th July, 1958

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faces of the parts. A thin nickel-containing layer is positioned between the titanium or titanium alloy parts to be joined and thereafter heated to a temperature high enough to cause sufficient intermetallic solid-solid diffusion of nickel into titanium and *vice versa* to form a eutectic of approximately 30% to 31% nickel which subsequently flows and fills the point. On continued heating at or above the eutectic point, the nickel in the nickel-titanium eutectic diffuses into the adjacent titanium members until all the nickel is dissolved in solid beta phase titanium and the eutectic phase com-

pickling in a hydrofluoric acid solution preferably of a concentration of about 2%. After the cleaned components have been assembled, the assembly is heated to a temperature above 1760° F., preferably above 1800° F. It is important that the titanium and nickel surfaces be clean initially and be maintained clean during heating, which therefore occurs in an atmosphere of an inert gas, such as purified argon or helium, in order to prevent oxidation of the readily oxidizable titanium parts. For the same reason the assembly is cooled in the same atmosphere. Argon is preferred because

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Price 3s. 6d.

Price 4s 6d

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Assembly of Titanium or Titanium Alloy Parts and method of Brazing same

We, GENERAL MOTORS CORPORATION, a company incorporated under the laws of the State of Delaware in the United States of America, of Grand Boulevard in the City of Detroit, State of Michigan, in the United States of America (assignees of Alfred Lindley Boegehold and Charles William Vigor), do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to brazed titanium metal assemblies and to methods of joining titanium or titanium alloy parts by a brazing process.

It is difficult to braze titanium or titanium base alloys due to the readily oxidizable nature of these materials and due to the formation of a brittle junction or interface between the titanium parts and the brazing material.

Accordingly the invention is concerned with a method of brazing a titanium assembly in which the titanium metal parts are securely bonded together without the formation of a brittle interface layer.

By the invention, a nickel-titanium alloy layer is diffused into the adjacent faces of the parts. A thin nickel-containing layer is positioned between the titanium or titanium alloy parts to be joined and thereafter heated to a temperature high enough to cause sufficient intermetallic solid-solid diffusion of nickel into titanium anl *vice versa* to form a eutectic of approximately 30% to 31% nickel which subsequently flows and fills the point. On continued heating at or above the eutectic point, the nickel in the nickel-titanium eutectic diffuses into the adjacent titanium members until all the nickel is dissolved in solid beta phase titanium and the eutectic phase completely disappears, whereupon no molten material exists in the joint. The resultant joint is strong, reasonably ductile, and possesses excellent resistance to shear. The scope of the invention is defined by the appended claims; and how it can be carried into effect is hereinafter particularly described with reference to the accompanying drawing, in which:—

Figure 1 is a fragmentary side view of a double shear brazing specimen having titanium parts which are joined together in accordance with the invention;

Figure 2 is a drawing of a photomicrograph of a brazed and partially diffused titanium joint using a nickel shim; and

Figure 3 is a drawing of a photomicrograph of a brazed and completely diffused titanium joint using a nickel shim in accordance with the invention.

A pair of titanium members 10 and 12 are to be joined at their ends by thinner titanium sheets 14 and 16. Very thin sheets 18 and 20 of nickel or nickel-base alloy are interposed between the titanium parts 10 and 14 and 10 and 16, respectively. Smaller nickel shims 22 and 24 are also positioned between the titanium parts 12 and 14 and 12 and 16 respectively.

The titanium parts are cleaned by pickling in a hydrofluoric acid solution preferably of a concentration of about 2%. After the cleaned components have been assembled, the assembly is heated to a temperature above 1760° F., preferably above 1800° F. It is important that the titanium and nickel surfaces be clean initially and be maintained clean during heating, which therefore occurs in an atmosphere of an inert gas, such as purified argon or helium, in order to prevent oxidation of the readily oxidizable titanium parts. For the same reason the assembly is cooled in the same atmosphere. Argon is preferred because

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it is heavier than air and can be conveniently employed to purge the furnace.

Although 1800° F. is a temperature considerably below the melting point of either nickel or titanium, it has been found that at this temperature there is sufficient intermetallic solid-solid diffusion of nickel into beta phase titanium to form a nickel-titanium alloy zone of sufficient nickel concentration to form a liquid eutectic phase of 30 to 31% nickel. That this is due to the diffusion of nickel into titanium rather than titanium into nickel is confirmed by observation that the diffusion rate of nickel into titanium is about 10 times that of titanium into nickel. Some nickel-rich titanium phases are formed during the diffusion but the amount of these phases is small and they are rapidly dissolved in the eutectic liquid.

It has been found that, when the amount of nickel is small relative to the amount of titanium present in the adjacent parts, the beta phase titanium has such a large absorptive capacity for the nickel that upon continued heating the eutectic is depleted of nickel until no zone of eutectic composition remains. At or above the eutectic temperature of approximately 1760° F., the resultant material is high-melting beta phase titanium having nickel in solid solution. Upon cooling to room temperature, the beta phase titanium undergoes a eutectic decomposition leaving alpha phase titanium and a Ti_2Ni compound phase whose amount and distribution is governed by the nickel concentration in the beta phase.

In positioning the components of the assembly, the titanium parts to be joined, such as sheet 14 and member 10, should overlap the nickel sheet, such as shim 18, by approximately $^1/_{32}$ of an inch or more at each edge. Such an overlap prevents the molten eutectic formed by the nickel and titanium parts from flowing outside the joint area. If the overlap is omitted and the eutectic is permitted to flow beyond the joint area, a certain amount of undercutting of the titanium components adjacent this joint may result due to the high solubility of the titanium in the eutectic.

A slight pressure is preferably applied to the assembled parts to maintain them in close contact, a pressure between one and three pounds per square inch usually being sufficient. Frequently the weight of the uppermost members is sufficient to form satisfactory contact and a sound joint.

When the assembly is heated in the inert atmosphere, the heating period is preferably between half an hour and three hours. Heating for one and a half hours at about 1850° F. has been found to give good results, although the temperature may vary from approximately 1760° F. to about 2400° F. However, 1900° F. is the normal practical upper limit of temperature. Within these limits the use of higher temperatures permits a decrease in the heating period necessary, while employment of lower temperatures necessitates a longer heating period.

The photomicrograph of which Figure 2 is a drawing, has a magnification of approximately fifty diameters and is of a metallographic specimen which was etched with a solution consisting of about 2% hydrofluoric acid, 12% nitric acid, 45% glycerol and the balance water. In this joint, which was specially formed to illustrate the brazing process according to the present invention, the nickel is only partially diffused into the titanium. In order to obtain this partial diffusion, a short heating time and a relatively thick nickel shim were used to form the joint. A heating period of approximately 45 minutes at the relatively low temperature of 1850° F. was employed.

Use of a temperature at the lower end of the temperature range is normally adequate if a very thin nickel sheet or shim is used or if, with a thicker nickel sheet, the heating period is sufficiently long to permit complete diffusion of the eutectic. The shim used was approximately 0.004 inches thick, and because of the short brazing time and/or the relatively low temperature, an appreciable amount of eutectic remained in the joint upon cooling. The eutectic 26 is formed in the centre of the joint at a location previously occupied by the nickel and is bounded on each side by layers 28 and 30 of nickel-titanium alloys which are hypereutectoid with respect to the nickel. Beyond the outer boundaries of the hypereutectoid layers are formed layers 32 and 34 which are hypoeutectoid with respect to the nickel content away from the joint area and gradually merge into the adjacent titanium base metal parts 36 and 38.

When a longer heating time is employed and/or a thinner nickel shim is used a joint is formed such as is shown in the photomicrograph of which Figure 3 is a drawing. This photomicrograph is a fifty diameter enlargement of a specimen prepared in the same way as the specimen shown in Figure 2. The specimen shown in Figure 3 was heated for approximately one and a half hours at 1860° F. The eutectic was initially

formed in the joint, but subsequent heating diffused the nickel into the titanium base metal and shifted the composition of the eutectic to a lower nickel concentration until the eutectic phase completely disappeared, leaving the titanium-rich, high-melting point beta phase. This latter phase transformed by a eutectoid decomposition to the alpha phase plus Ti_2Ni compound on cooling of the joint to room temperature. It is desirable to eliminate the eutectic from the joint because the eutectic is relatively brittle and would seriously weaken the joint if it were permitted to remain therein. The resultant joint, therefore, consists of a hypereutectoid area 40 bounded by hypoeutectoid zones 42 and 44 between the initial titanium base metal compositions 46 and 48.

As can be seen in Figure 3, the joint formed in accordance with the invention possesses no sharp lines of demarcation between the titanium, the hypereutectoid area and the hypoeutectoid zones. Hence, no brittle interface exists in this joint and it possesses exceptionally high strength. The hypereutectoid area preferably has a thickness between 0.0025 and 0.02 inches, while the optimum thickness of each of the hypereutectoid areas is between 0.0075 inches and 0.04 inches. It will be appreciated, of course, that the extent of the markings indicating the zones is only approximate and that portions of one zone actually extend into adjacent zones varying distances at different positions.

In order that the nickel layer between the adjacent parts may be completely absorbed by the latter without the formation of the brittle eutectic, the shims employed must be sufficiently thin to eliminate the possibility of retention of the eutectic in the joint. In general, the nickel shims should have a thickness between 0.0002 inches and 0.003 inches, depending on the size of the parts to be joined, the desired strength of the joint and practicality of heating ranges and times. While it has been found that, in some instances, these shims may be even thinner than 0.0002 inches, it rarely is desirable to use a shim thicker than 0.003 inches because of the difficulty of absorbing the additional nickel. To provide homogeneity and strength to the joint, it is normally preferable to employ shims having a thickness between 0.001 inches and 0.0015 inches. The shim thicknesses have been exaggerated in Figure 1 in order more clearly to show the construction of this brazing specimen. Actually, nickel sheets having the aforementioned dimensions are in the form of a thin, flexible foil. Shims of the desired shim thickness can be obtained from thicker sheets by cold rolling.

The layer of nickel or nickel-containing alloy can be applied to the titanium or titanium-base alloy members to be brazed by means of a metal spray gun; or a nickel or nickel-containing powder may also be used as the brazing material. In general, the particle size of the metallic powder should be between 100 and 300 mesh, although somewhat finer powders are usually also satisfactory.

A titanium-base alloy having a nickel content between 13% and 38% may be satisfactorily used in powder form, and in some instances nickel-titanium alloys having somewhat higher nickel contents may be employed. If a powdered alloy of this type has a nickel content which is very much less than the nickel content in the eutectic composition, however, capillary action of the brazing material may be detrimentally affected. Moreover, when nickel-titanium alloy compositions are used which differ very considerably from the eutectic composition, the cast alloy is insufficiently brittle to be easily pulverized into powder form. Hence it is desirable that such nickel content be within the aforementioned range. A powdered nickel-titanium alloy containing approximately 30% nickel and the balance substantially all titanium, which composition corresponds approximately to the eutectic mixture, has been found to provide a very sound joint.

It will be understood that pure nickel powder or other high nickel-content powders may be used instead of a nickel-titanium alloy powder or can be added to the latter to provide a brazing powder having a nickel content considerably above 38%. Thus it can be seen that when the brazing layer is applied in powder form, the powder composition can be varied by the use of nickel or nickel base alloys to produce a brazing powder having a nickel content as high as 100%.

If a nickel-containing powder is to be used, it is preferably mixed with a volatile lacquer which vaporizes upon heating, this mixture being used in the form of a viscous liquid or paste. Such a paste may be applied as a fillet at the edge of overlapping titanium components and upon melting is drawn into the joint by capillary action. When a nickel-titanium powder approximately the eutectic composition is employed, the preliminary solid-solid diffusion is not needed to form the eutectic because the eutectic has been supplied as the powder. Normally the thickness of the paste of powder layer

should approximately correspond to the thickness of the nickel base shims hereinbefore described.

In order to form a joint having high strength and reasonable ductility, it is normally desirable to employ nickel metal of high purity containing not in excess of approximately 0.02% carbon, particularly if used in shim form. However, nickel-containing alloys, such as nickel-titanium alloys, can also be used if the nickel content is sufficiently high. Small amounts of other alloying elements, such as iron, aluminium, boron, carbon, chromium, silicon, manganese and silver, may also be present in the powdered alloy without detrimental results provided they do not adversely affect the melting point to too great an extent. For optimum results, however, it appears that these alloying elements should not be present in nickel-titanium alloy powders in amounts greater than approximately 15%.

Nickel-containing bonding layers can be used if they contain a sufficient amount of nickel to provide the necessary diffusion and this nickel content may be as low as 13%. However, when a solid shim or sheet is employed in this brazing operation, a nickel-titanium alloy in which the titanium is the major constituent is normally too brittle to be rolled, and a practical shim composition is one which gives a sufficiently ductile sheet to permit it to be rolled to the appropriate thickness and used in sheet form.

Although titanium-base alloys in general may be employed in the present invention, excellent results are obtained with respect to shear strength when a commercially pure metal is used. An example of a commercially available titanium alloy is one composed of approximately 0.1% iron, 0.08% tungsten, 0.02% nitrogen, carbon not in excess of 0.04%, a trace of oxygen, and the balance substantially all titanium. Commercial titanium base alloys containing chromium, usually between 1.5% and 3%, may likewise be used. Thus an alloy composed of about 2.7% chromium, approximately 1.3% iron, 0.25% oxygen, 0.02% nitrogen, tungsten not in excess of 0.04%, 0.02% carbon, and the balance titanium has proved to be satisfactory. Commercially available alloys may also be obtained with manganese contents as high as 7% and aluminium contents up to 5%. It is likewise possible to achieve excellent results and to form a sound joint when joining titanium-nickel alloys. If such a nickel-containing titanium alloy is employed, however, it is preferable to maintain the nickel content below 31%, and for optimum results the alloy preferably should not contain more than 7% nickel.

When subjected to shear tests in a tensile machine, joints formed by brazing in accordance with the present invention exhibited shear strength in excess of 40000 pounds per square inch. In genral, failure occurred partly in the joint area and partly in the titanium base metal itself. However, in many instances the failure occurred by tension only in the centre joint component 10 or 12 outside the brazed area, while in other cases failure took place on one side of the joint by shear and on the other side by tensile failure of one of the overlapping components 14 and 16. The joints exhibited shear strengths considerably above those heretofore obtained with other methods of brazing titanium parts.

It will be understood that the term "titanium metal" is used to include pure titanium, commercially pure titanium and titanium-base alloys.

The heating of titanium above the alpha phase to the beta phase transformation temperature, which is approximately 1620° F., usually results in grain growth; the higher the temperature the more pronounced this grain growth becomes. Although the resultant larger grain size does not materially affect the tensile strength of the joint, it does result in lowering the ductility of the titanium metal.

However, the alloy layers produced in nickel-brazed joints in accordance with the invention are susceptible to heat treatment to produce greater strength and ductility, as well as increased hardness. For example, it has been found that, upon heating and quenching the formed nickel-titanium alloy compositions in water, or other suitable media, from temperatures in the beta phase region, preferably between 1400° F. and 1800° F., a martensitic type reaction occurs in the hypo-eutectoid area. While neither of these phases shows an appreciable increase in hardness as quenched, tempering at a temperature between 400° F. and 1400° F. results in greater hardness and strength due to ageing of the martensitic type phase and decomposition of the retained beta phase. Likewise, the ductility of the alloy zone is increased as a result of such heat treatment because the lamellar structure found in the "as-brazed" condition is thereby eliminated. In general, a tempering temperature of approximately 600° F. appears to give best results.

What we claim is:—

1. A method of bonding parts of titanium or titanium alloy which com-

prises placing a nickel-containing layer between the surfaces of the parts to be joined and heating the parts and layer to diffuse the nickel in the layer into the titanium metal parts to bond the parts together.

2. A mehod of forming a joint between titanium of titanium alloy parts which comprises interposing a layer having a high nickel content between the titanium metal parts and heating the parts and layer to a temperature between 1760° F. and 2400° F. to diffuse the nickel in the layer into the surfaces of the titanium metal parts to bond the parts together.

3. A method according to Claim 2, wherein the parts and layer are heated to a temperature between 1800° F. and 1900° F.

4. A method according to Claim 3, wherein the parts and layer are heated for between half an hour and three hours.

5. A method according to Claim 4, wherein the temperature is between 1850° F. and 1860° F. and the period of heating is about one and a half hours.

6. A method according to Claim 2, 3, 4 or 5, wherein the parts are heated in an atmosphere of inert gas and are subsequently cooled in this atmosphere.

7. A method according to Claim 6, wherein the inert gas is argon.

8. A method according to any of the preceding claims in which the nickel-containing layer is applied to at least one of the titanium or titanium alloy parts by spraying with a metal spray gun.

9. A method according to any of the preceding claims, in which the nickel-containing layer is formed by applying a powdered titanium-nickel brazing alloy to the juncture of the titanium or titanium alloy parts and thereafter heating the parts until the powdered brazing alloy melts and is drawn into the joint area by capillary attraction, whereupon absorption of nickel into the titanium or titanium alloy parts from the molten brazing alloy transforms the molten phase to a solid phase to securely bond the parts together.

10. A method according to any of the preceding claims in which the titanium or titanium alloy parts, prior to joining, are cleaned by pickling in a dilute hydrofluoric acid solution.

11. A method according to any of the preceding claims in which the titanium or titanium alloy parts and nickel-containing layer are held in close contact by slight positive pressure.

12. A method according to any of the preceding claims wherein the nickel-containing layer has a thickness between 0.0002 and 0.003 inches.

13. A method according to Claim 12, wherein the thickness of the layer is between 0.001 and 0.0015 inches.

14. A method according to any of the preceding claims in which the nickel-containing layer is a powdered titanium-nickel brazing alloy containing between 13% and 38% nickel.

15. A method according to Claim 14, in which the nickel content of the alloy is between 30 and 31%.

16. A method according to any of the preceding claims in which the nickel containing layer is a powdered titanium-nickel brazing alloy having a particle size between 100 mesh and 300 mesh.

17. A method of brazing titanium or titanium alloy parts together by means of a nickel base alloy which comprises cleaning the titanium or titanium alloy parts to be joined by pickling in a dilute acid solution, interposing a sheet of nickel base alloy between the parts in direct contact with the adjacent surfaces thereof, maintaining a slight positive pressure on the parts to hold the nickel base alloy sheet securely in position therebetween, subsequently heating the assembled titanium or titanium alloy parts and nickel base alloy sheet in an atmosphere of argon gas for between half an hour and three hours at a temperature between 1800° F. and 1900°., thereafter permitting the formed assembly to cool in the atmosphere, reheating the assembly for a short time at a temperature between 1400° F. and 1800° F., quenching the reheated assembly, and finally tempering the quenched assembly at a temperature between 400° F. and 1400° F.

18. A brazed assembly comprising titanium or titanium alloy parts joined together by a nickel-titanium alloy layer which is diffused into the adjacent faces of the titanium or titanium alloy parts.

19. An assembly according to Claim 18 in which the nickel-titanium layer comprises a titanium-nickel hypereutectoid zone bounded on each side by a titanium-nickel hypoeutectoid zone.

20. A method of bonding parts of titanium or titanium alloy, substantially as particularly described herein.

21. A brazed assembly of titanium or titanium alloy parts, substantially as particularly described herein.

E. WILLIAMSON,
Chartered Patent Agent.

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Published at the Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

746,648 COMPLETE SPECIFICATION
1 SHEET
This drawing is a reproduction of the Original on a reduced scale.

FIG. 1.

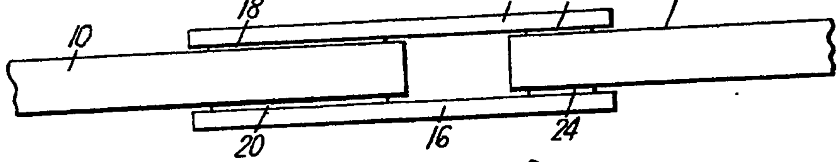

FIG. 2.

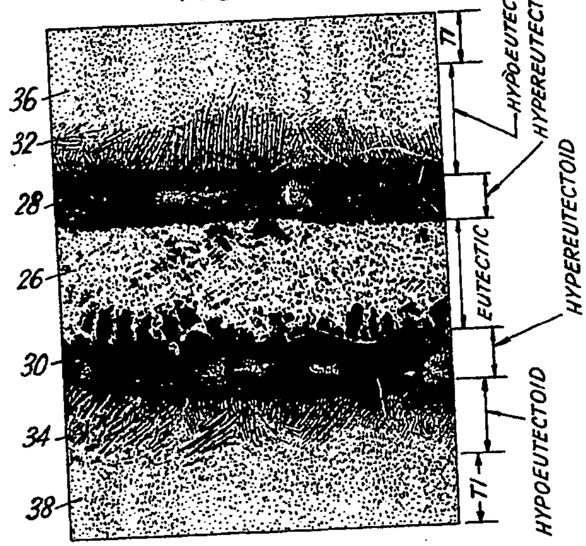

FIG. 3.